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THE ELECTROCHEMISTRY OF ORGANOPHOSPHORUS COMPOUNDS(U)
AUBURN UNIV AL J H HOWARD 28 JAN 88 N88014-81-K-8846

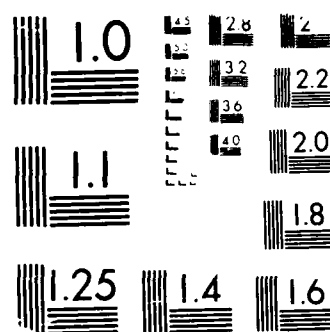
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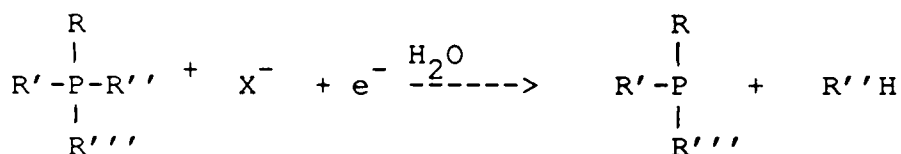
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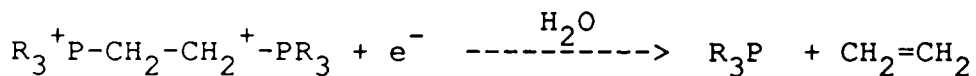
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THE ELECTROCHEMISTRY OF ORGANOPHOSPHORUS COMPOUNDS

The goal of this project was to study the electrochemical behavior of organophosphorus compounds with a particular interest in exploring and developing the synthetic potential of this technique. The first phase of the project focused upon the reduction of phosphonium salts. Previous reports in the literature indicated that the reduction of phosphonium salts in aqueous media led to phosphines:



We attempted the synthesis of the important chelating ligands, $\text{R}_2\text{PCH}_2\text{CH}_2\text{PR}_2$, by the method shown below but found that ethelene was preferentially extruded resulting in the formation of tertiary monophosphines.



A study of the mechanism of the phosphonium salt reduction was initiated and since the aqueous solvent was electrochemically active at potentials positive of the phosphonium salt reduction, a study in nonaqueous potentials was initiated. An unexpected result of this study was that the products were changed and that ylide formation in virtually quantitative yield was observed. Details of these results have been given in previous reports and were presented at the Southeastern Regional ACS Meeting in Charlotte, N. C. in Nov, 1983 (abstract attached). These results and additional mechanistic

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insights were also reported at the 189th ACS Meeting in Miami Beach, Florida in April of 1985 (abstract attached).

The second phase of this project was to investigate the reductive electrochemical cleavage of labile phosphorus halogen bonds in compounds of the type R_2P-X and $R_2P(O)-X$ where X is F, Cl, Br, and O-Ph. These reductions were found to result in the formation of the dimeric products, R_2P-PR_2 and $R_2P(O)-P(O)R_2$ respectively. Mechanistic studies by cyclic voltammetry, controlled potential coulometry and product analysis have been interpreted to indicate that formation of the product proceeded via an anionic intermediate. These results have been reported at the 189th ACS Meeting in Miami Beach, FL in April of 1985 (trivalent compounds, abstract attached) and at the 192 ACS Meeting in Anaheim, CA in September of 1986 (pentavalent compounds, abstract attached) and a report of the trivalent compounds study has appeared in the Journal of Organic Chemistry, 1986, 51, 4185. (Technical Report 1).

The above research comprised the Ph.D. dissertation of T. J. Hall who received his degree in June of 1986. (Dissertation Abstract attached).

Phase three of the project involved an investigation of the electrocatalytic oxidation by dioxygen of tertiary phosphorus compounds of the series $R_{3-n}P(O-R)_n$ where n was equal to 0, 1, 2, and 3. We found that the electrode initiated a presumably free radical process with a chain length critically dependant upon the value of n. This research formed the basis of the M. S. thesis of Mr. Hun-Lin Ho who received his degree in December of 1987 (M. S. Thesis Abstract attached).

Progress has also been made in investigating the electrochemical reduction of compounds of the type $R-PX_2$ in nonaqueous solvents. We have shown that the products of this reduction are the cyclic oligimers of the form $(R-P)_n$ where n is equal to 3, 4, and 5. Two possible mechanisms for the formation of the products include the intermediacy of the phosphorus analog of carbenes, $R-P$, and the P-P doubly bonded "phosphenes" $R-P=P-R$. Experiments designed to differentiate these pathways and explore the mechanism of these reactions are being conducted by Mr. John Griggs who should receive his Ph.D. during 1988.

ELECTROCHEMICAL REDUCTION OF ORGANOPHOSPHORUS COMPOUNDS: PRODUCTS AND MECHANISM
OF PHOSPHONIUM SALTS CAPABLE OF YLIDE FORMATION

T.J. Hall and J.H. Hargis*

Contribution from the Department of Chemistry, Auburn University, Auburn
University, Alabama 36849

The electrochemical reduction of phosphonium salts with a hydrogen on a carbon α to the phosphorus has been investigated using cyclic voltammetry, controlled-potential coulometry, and product analysis. Using dry acetonitrile and N,N-dimethyl formamide as solvents, the reduction appears to proceed by a one electron transfer forming the ylide with concurrent adsorption of hydrogen on the electrode surface. Mechanistic views are further developed with the addition of water resulting in the formation of triphenylphosphine, triphenylphosphine oxide, and the corresponding hydrocarbon.

ABSTRACTS

35th Southeastern Regional Meeting
American Chemical Society



Charlotte, North Carolina
November 9, 10, 11, 1983

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chloroform. In the absence of a proton source, the resultant trichloromethyl anion decomposes to dichlorocarbene which is identified by trapping of reaction products. Under conditions corresponding to those of a Michaelis-Arbuzov reaction the diallyl phosphorodichloridate is generated as it is under the standard conditions for the Todd reaction.

- 468 THE EFFECTS OF SOME ELECTRON WITHDRAWING GROUPS IN THE 1-POSITION OF PYRROLE TOWARDS ELECTROPHILES. Helmut M. Gilow, Richard P. Hodge, and Yoon Hee Hong, Department of Chemistry, Southwestern At Memphis, Memphis, TN 38112.

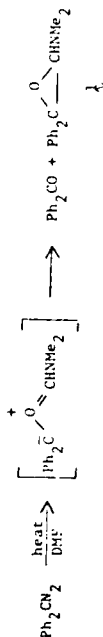
Electrophilic substitution of pyrroles occurs predominantly in the 2-position but under certain conditions varying amounts of substitution also occur in the 3-position making it difficult to obtain pure products. We have found that electron withdrawing groups in the 1-position have a significant effect on 2/3 ratios in some electrophilic substitutions.

Pyrroles with substituents in the 1-position such as CH_3SO_2 -, CF_3SO_2 -, and R_3N - have been synthesized. Nitration of these pyrroles occur predominantly, and in some cases exclusively, in the 3-position. Friedel-Crafts acylation can be carried out under conditions where 2-substitution or 3-substitution is the predominant product. Bromination with NBS in THF occurs exclusively in the 2-position. Deuterium exchange in deuterated trifluoroacetic acid was found to occur more rapidly in the 2-position. The results from these and other electrophilic substitutions will be rationalized in terms of the mechanism of the reaction.

Important synthetic applications of these reactions will be discussed.

- 469 CARBONYL YLIDE FORMATION IN DMF. Suzanne T. Purrington and Grant B. Kenlon, Department of Chemistry, North Carolina State University, Raleigh, N.C. 27650.

The major product of decomposition of diphenyldiazomethane in DMF is benzophenone. It is thought to arise from interaction of the electrophilic diphenylcarbene with the carbonyl oxygen of DMF to form a carbonyl ylide. Further evidence for ylide formation is obtained by observation of oxirane λ in the reaction mixture.



- 470 ELECTROCHEMICAL GENERATION OF WITTIG REAGENTS. T. J. Hall and J. H. Hargis, Dept. of Chemistry, Auburn University, AL 36849

The electrochemical reduction of phosphonium bromide salts at a platinum cathode in dry acetonitrile or dimethylformamide leads to the formation of phosphorus ylides in good yields. The inclusion of aldehydes or ketones in the solution allows a direct convenient preparation of alkenes via the Wittig reaction. Evidence will be presented which indicates that a direct reduction of the phosphonium salt at the electrode surface leads to ylide formation with concurrent adsorption of hydrogen on the platinum surface. The addition of small amounts of water or alcohol dramatically alters the product distribution and leads to phosphine formation. Mechanistic implications of these observations will be discussed.

- 471 THE REACTIONS OF ATOMIC CARBON WITH SIMPLE AMINES. Philip B. Shevlin and Daniel W. McPherson, Department of Chemistry, Auburn University, AL 36849

ARC generated carbon atoms have been reacted with simple amines by cocondensing the two species on a matrix at 77°K. The reaction of carbon with amines leads to products of both N-H and C-N insertion (imines) as well as products of C-H insertion (unsaturated amines). In addition, C(p) appears to form a stable complex upon reaction with certain amines. Some reactions of this complex, which has a measurable lifetime at 77°K, will be discussed.

- 472 THE POSSIBLE INVOLVEMENT OF EXCITED SINGLET METHYLENE IN THE DEOXYGENATION OF FORMALDEHYDE BY ATOMIC CARBON. Sheikh N. Ahmed and Philip B. Shevlin, Department of Chemistry, Auburn University, AL 36849

Carbon atoms, generated by the thermolysis of 5-diazotetrazole, react with formaldehyde to generate methylene which has been trapped with cyclohexene and 2,2-butene.

A DIVISION OF Organic Chemistry

B TITLE OF PAPER Electrochemical Reduction of Organophosphorus Compounds:
Mechanism and Products from Phosphorus-Halogen Bond
Cleavage

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ELECTROCHEMICAL REDUCTION OF ORGANOPHOSPHORUS COMPOUNDS: MECHANISM AND PRODUCTS
FROM PHOSPHORUS-HALOGEN BOND CLEAVAGE. T.J. Hall and J.H. Hargis. Department
of Chemistry, Auburn University, AL 36849

The electrochemical cleavage of phosphorus-halogen bonds in chlorodiphenylphosphine and bromodiphenylphosphine in dry acetonitrile solution has been accomplished with the formation of tetra-phenylbiphosphine as the exclusive product. A mechanism which involves the intermediacy of diphenylphosphinyl anions is suggested based on cyclic voltammetry and controlled potential coulometry studies. Attempts to utilize these intermediates in the synthesis of tertiary phosphines will be discussed.

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ELECTROCHEMICAL REDUCTION OF PENTAVALENT ORGANOPHOSPHORUS
COMPOUNDS: MECHANISMS OF AND PRODUCTS FROM PHOSPHORUS-HETEROATOM
BOND CLEAVAGE

T. J. Hall and J. H. Hargis

Contribution from the Department of Chemistry, Auburn
University, Alabama 36849

Abstract: The electrochemical cleavage of phosphorus-halogen or phosphorus-oxygen bonds in compounds of the type $\text{Ph}_2\text{P}(\text{O})\text{X}$ where $\text{X} = \text{F}, \text{Cl}, \text{Br},$ and OPh , has been studied in acetonitrile solution. An examination of cyclic voltammetry data and controlled potential coulometry studies allows the postulation of anionic intermediates leading to the formation of the products of the reaction. The exclusive stable product is tetraphenyldiphosphinedioxide, but evidence will be discussed concerning evidence for a quasi-stable mixed anhydride intermediate.

DISSERTATION ABSTRACT
ELECTROCHEMICAL REDUCTION OF ORGANOPHOSPHORUS
COMPOUNDS: PRODUCTS AND MECHANISMS OF
PHOSPHONIUM, TRIVALENT, AND
PENTAVALENT COMPOUNDS

Timothy Jack Hall

Doctor of Philosophy, June 6, 1986
(B.S., University of Montevallo, 1982)

125 Typed Pages

Directed by J. Howard Hargis

The mechanisms of the electrochemical reduction of phosphonium, trivalent, and pentavalent organophosphorus compounds in non-aqueous systems have been proposed based on the results of cyclic voltammetry, controlled potential coulometry, and trapping experiments.

The mechanism of the electrochemical reduction of quaternary phosphonium salts was found to be dependent upon whether or not the carbon α to the phosphorus has a hydrogen atom. The salts with such a hydrogen were found to form the corresponding phosphonium ylide upon reduction in the dry solvents. On the other hand, salts such as tetraphenylphosphonium bromide find ylide formation impossible and electrolytically cleaved to the tertiary phosphine and the corresponding hydrocarbon. Particular

reference was given to the phosphonium salts capable of ylide formation. The electrochemical reduction of benzyl-, n-propyl-, ethyl-, and methyltriphenylphosphonium ions in the dry solvents was shown to proceed by a one electron reduction to give the exclusive ylide product. Furthermore, carbonyl compounds were added to the electrolyses to react with the electrochemically-generated ylides via the Wittig reaction. The resulting olefins were found to catalytically isomerize from the Z isomer to the E isomer upon reduction.

The role of water in the reduction process of these phosphonium salts was investigated by adding D_2O to the previously dry solvents. In the case of benzyltriphenylphosphonium bromide, the presence of the tri- and di-deuterated species of toluene illustrated the basicity of the initially formed ylide.

Electrolyses of the trivalent and pentavalent organophosphorus compounds of the type Ph_2PX and $Ph_2P(O)X$ ($X = Br, Cl, F, OPh$) in dry acetonitrile were accomplished with the formation of the respective dimer as the exclusive product. Cyclic voltammetric studies featuring the relationship between the concentration and peak current of both compounds indicated the intermediacy of the corresponding anion. The biphosphine products were proposed to result from nucleophilic attack of the intermediate anions on the starting material.

THESIS ABSTRACT
A STUDY OF THE ELECTROCATALYZED OXIDATION
OF TRIVALENT PHOSPHORUS COMPOUNDS
WITH DIOXYGEN

Hun Lin Ho

Master of Chemistry, December 12, 1987

(B.S., Tamkang University, 1978)

66 Typed Pages

Directed by J. Howard Hargis

Electrolyses of the trivalent organophosphorus compounds of the type $\text{Ph}_{3-x}\text{P}(\text{PhO})_x$ ($x=0,2,3$) in dry acetonitrile saturated with oxygen resulted in the formation of corresponding oxide compound. Two types of mechanisms have been proposed based on the results of cyclic voltammetry, controlled potential coulometry and trapping experiments. The results of electrolysis of triphenylphosphine produces 9 molecules of triphenylphosphine oxide per electron transferred. This suggests a chain mechanism operative in these reactions.

In the first mechanism proposed, a electrochemically formed phosphinium cation radical reacts with a second

molecule of trivalent compound to form dimer cation radical which undergoes dioxygen addition, subsequent addition of a second dimer cation radical and O-O bond cleavage to form corresponding oxide compound and initial phosphinium cation radical which continues the chain process. In the second mechanism proposed, initial formation of phosphinium cation radical then undergoes dioxygen addition with a subsequent addition of a second molecule of starting material, O-O bond cleavage, and electron transfer from starting material to the oxidized cation radical product.

These electrolysis results also show that the order of reactivity is $\text{Ph}_3\text{P} > (\text{PhO})_2\text{PhP} > (\text{PhO})_3\text{P}$. The order of oxidation potentials of trivalent organophosphorus compounds is $(\text{PhO})_3\text{P} > (\text{PhO})_2\text{PhP} > (\text{PhO})\text{Ph}_2\text{P} > \text{Ph}_3\text{P}$. Interestingly, the order of oxidation potentials of pentavalent compounds is $\text{Ph}_3\text{PO} > (\text{PhO})_2\text{PhPO} > (\text{PhO})_3\text{PO}$ which is just reversed from the trend observed in the trivalent organophosphorus compound.

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